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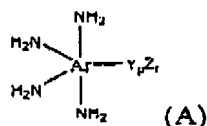
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Claims

29. A proton-conducting polymer membrane which comprises polyazoles containing phosphonic acid groups and is obtainable by a process comprising the steps:

- 5 A) mixing one or more aromatic or heteroaromatic tetraamino compounds with one or more aromatic or heteroaromatic carboxylic acids or derivatives thereof which contain at least two acid groups per carboxylic acid monomer, with at least part of the tetraamino compounds or the carboxylic acids comprising at least
- 10 one phosphonic acid group, or mixing of one or more aromatic or heteroaromatic diaminocarboxylic acids, of which at least part comprises phosphonic acid groups, in polyphosphoric acid to form a solution or dispersion;
- 15 B) optionally heating the solution or dispersion obtained according to step A) under inert gas to temperatures of up to 350°C to form polyazole polymers;
- 20 C) applying a layer using the mixture from step A) or B) to a support, thus forming a membrane on the support; and
- D) partially hydrolyzing the polyphosphoric acid moieties of the membrane from step C) until the membrane is self-supporting.

25 30. The membrane of Claim 29, characterized in that the mixture prepared in step A) comprises aromatic or heteroaromatic tetraamino compounds of the formula (A)

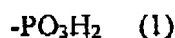


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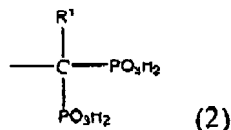
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where

- Ar is an aromatic or heteroaromatic group,
 Y is a bond or a group having from 1 to 20 carbon atoms,
 p is an integer from 1 to 4 and represents the number of
 bonds or groups Y via which the group Z is
 bound to the group Ar,
 r is an integer from 1 to 4 and represents the number of
 groups Z which are bound to the group Y or, if
 Y is a bond, to the aromatic or heteroaromatic
 group Ar, and
 Z is a group of the general formula (1)

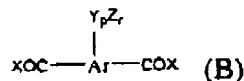


or the general formula (2)



where R^1 is a hydrogen atom or a group having from 1 to 20 carbon atoms.

31. The membrane of Claim 29, characterized in that the mixture prepared in step A) comprises aromatic or heteroaromatic carboxylic acids of the formula (B)



where

- Ar is an aromatic or heteroaromatic group,
 X is a halogen atom or a group of the formula OR^2 , where R^2 is a hydrogen atom or a group having from 1 to 20 carbon atoms,

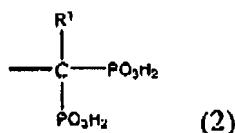
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Y is a bond or a group having from 1 to 20 carbon atoms,
 p is an integer from 1 to 4 and represents the number of bonds or
 groups Y via which the group Z is bound to the group
 Ar,
 5 r is an integer from 1 to 4 and represents the number of groups
 Z which are bound to the group Y or, if Y is a bond, to
 the aromatic or heteroaromatic group Ar, and
 Z is a group of the general formula (1)

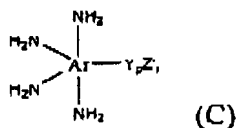


10 or the general formula (2)



where R^1 is a hydrogen atom or a group having from 1 to 20 carbon
 atoms.

32. The membrane of Claim 29, characterized in that the mixture
 15 prepared in step A) comprises aromatic or heteroaromatic
 tetraamino compounds of the formula (C)



where

Ar is an aromatic or heteroaromatic group,
 20 Y is a bond or a group having from 1 to 20 carbon atoms,
 p is an integer from 1 to 4 and represents the number of
 bonds or groups Y via which the group Z is
 bound to the group Ar,

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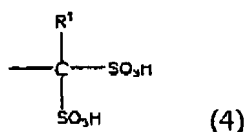
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r is an integer from 1 to 4 and represents the number of groups Z which are bound to the group Y or, if Y is a bond, to the aromatic or heteroaromatic group Ar , and

Z' is a group of the general formula (3)

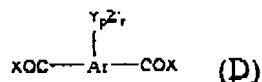


or the general formula (4)



where R^1 is a hydrogen atom or a group having from 1 to 20 carbon atoms.

33. The membrane of Claim 29, characterized in that the mixture prepared in step A) comprises aromatic or heteroaromatic carboxylic acids of the formula (D)



where

Ar is an aromatic or heteroaromatic group which optionally bears further substituents,

X is a halogen atom or a group of the formula OR^2 , where R^2 is a hydrogen atom or a group having from 1 to 20 carbon atoms,

Y is a bond or a group having from 1 to 20 carbon atoms,

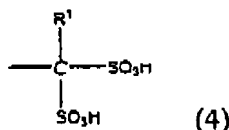
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- p is an integer from 1 to 4 and represents the number of bonds or groups Y via which the group Z is bound to the group Ar,
- r is an integer from 1 to 4 and represents the number of groups Z which are bound to the group Y or, if Y is a bond, to the aromatic or heteroaromatic group Ar, and
- Z' is a group of the general formula (3)



or the general formula (4)



where R¹ is a hydrogen atom or a group having from 1 to 20 carbon atoms.

34. The membrane of Claim 29, characterized in that the mixture prepared in step A) comprises aromatic or heteroaromatic tetraamino compounds which contain no phosphonic acid groups and aromatic or heteroaromatic carboxylic acids which contain at least one phosphonic acid group.
35. The membrane of Claim 29, characterized in that the mixture prepared in step A) comprises 3,3',4,4'-tetraaminobiphenyl, 2,3,5,6-tetraaminopyridine, or 1,2,4,5-tetraaminobenzene.
36. The membrane of Claim 29, characterized in that the mixture prepared in step A) comprises isophthalic acid, terephthalic acid, phthalic acid, 5-hydroxyisophthalic acid, 4-hydroxyisophthalic acid, 2-hydroxyterephthalic acid, 5-aminoisophthalic acid, 5-N,N-dimethylaminoisophthalic acid,

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5-N,N-diethylaminoisophthalic acid, 2,5-dihydroxyterephthalic acid, 2,5-dihydroxyisophthalic acid, 2,3-dihydroxyisophthalic acid, 2,3-dihydroxyphthalic acid, 2,4-dihydroxyphthalic acid, 3,4-dihydroxyphthalic acid, 3-fluorophthalic acid, 5-fluoroisophthalic acid, 2-fluoroterephthalic acid, tetrafluorophthalic acid, tetrafluoroisophthalic acid, tetrafluoroterephthalic acid, 1,4-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, diphenic acid, 1,8-dihydroxynaphthalene-3,6-dicarboxylic acid, bis(4-carboxyphenyl) ether, benzophenone-4,4'-dicarboxylic acid, bis(4-dicarboxyphenyl) sulfone, biphenyl-4,4'-dicarboxylic acid, 4-trifluoromethylphthalic acid, 2,2-bis(4-carboxyphenyl)hexafluoropropane, 4,4'-stilbenedicarboxylic acid, 4-carboxycinnamic acid, or their C1-C20-alkyl esters or C5-C12-aryl esters, or their acid anhydrides or acid chlorides.

37. The membrane of Claim 29, characterized in that the mixture prepared in step A) comprises 2,3-diamino-5-carboxyphenylphosphonic acid, 2,3-diamino-6-carboxyphenylphosphonic acid, and 3,4-diamino-6-carboxyphenylphosphonic acid.

38. The membrane of Claim 29, characterized in that the mixture prepared in step A) comprises 2,3-diamino-5-carboxyphenylsulfonic acid, 2,3-diamino-6-carboxyphenylsulfonic acid, and 3,4-diamino-6-carboxyphenylsulfonic acid.

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39. The membrane of Claim 29, characterized in that the mixture prepared in step A) comprises aromatic tricarboxylic acids, their C1-C20-alkyl esters or C5-C12-aryl esters or their acid anhydrides or their acid halides or tetracarboxylic acids, their C1-C20-alkyl esters or C5-C12-aryl esters or their acid anhydrides or their acid halides.
40. The membrane of Claim 39, characterized in that the mixture prepared in step A) comprises: 1,3,5-benzenetricarboxylic acid (trimesic acid), 2,4,5-benzenetricarboxylic acid (trimellitic acid), (2-carboxyphenyl)iminodiacetic acid, 3,5,3'-biphehyltricarboxylic acid, 3,5,4'-biphenyltricarboxylic acid, 2,4,6-pyridinetricarboxylic acid, benzene-1,2,4,5-tetracarboxylic acid, naphthalene-1,4,5,8-tetracarboxylic acid, 3,5,3',5'-biphenyltetracarboxylic acid, benzophenonetetracarboxylic acid, 3,3',4,4'-biphenyltetracarboxylic acid, 2,2',3,3'-biphenyltetracarboxylic acid, or 1,2,5,6-naphthalenetetracarboxylic acid.
41. The membrane of Claim 39, characterized in that the content of tricarboxylic acid or tetracarboxylic acids is in the range of from 0 to 30 mol% based on dicarboxylic acid used.
42. The membrane of Claim 41, characterized in that the content of tricarboxylic acid or tetracarboxylic acids is in the range of from 0.1 to 20 mol% based on dicarboxylic acid used.
43. The membrane of Claim 42, characterized in that the content of tricarboxylic acid or tetracarboxylic acids is in the range of from 0.5 to 10 mol% based on dicarboxylic acid used.

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44. The membrane of Claim 29, characterized in that the mixture prepared in step A) comprises heteroaromatic dicarboxylic acids, tricarboxylic acids or tetracarboxylic acids which contain at least one nitrogen, oxygen, sulfur, or phosphorus atom in the aromatics.
45. The membrane of Claim 44, characterized in that pyridine-2,5-dicarboxylic acid, pyridine-3,5-dicarboxylic acid, pyridine-2,6-dicarboxylic acid, pyridine-2,4-dicarboxylic acid, 4-phenyl-2,5-pyridinedicarboxylic acid, 3,5-pyrazoledicarboxylic acid, 2,6-pyrimidinedicarboxylic acid, 2,5-pyrazinedicarboxylic acid, 2,4,6-pyridinetricarboxylic acid, benzimidazole-5,6-dicarboxylic acid or their C1-C20-alkyl esters or C5-C12-aryl esters or their acid anhydrides or their acid chlorides are used.
46. The membrane as claimed in claim 29, characterized in that the mixture prepared in step A) comprises diaminobenzoic acid or its monohydrochloride and dihydrochloride salts.
47. The membrane of Claim 29, characterized in that the heating according to step B) is carried out after the formation of a sheet-like structure according to step C).
48. The membrane as claimed in claim 29, characterized in that the solution produced in step A) or step B) further comprises dispersed or suspended polymer.
49. The membrane of Claim 29, characterized in that the treatment according to step D) is carried out at temperatures in the range of from 0°C to 150°C in the presence of moisture.

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50. The membrane of Claim 29, characterized in that the treatment of the membrane in step D) is carried out from 10 seconds to 300 hours.
51. The membrane of Claim 29, characterized in that the membrane formed after step D) is crosslinked by action of oxygen.
52. The membrane of Claim 29, characterized in that a layer having a thickness of from 20 to 4000 μm is produced in step C).
53. The membrane of Claim 29, characterized in that the membrane formed after step D) has a thickness of from 15 to 3000 μm .
54. An electrode having a proton-conducting polymer coating which is based on polyazoles and is obtainable by a process comprising the steps:
- A) mixing one or more aromatic or heteroaromatic tetraamino compounds with one or more aromatic or heteroaromatic carboxylic acids or derivatives thereof which contain at least two acid groups per carboxylic acid monomer, with at least part of the tetraamino compounds or the carboxylic acids comprising at least one phosphonic acid group, or mixing of one or more aromatic or heteroaromatic diaminocarboxylic acids, of which at least part comprises phosphonic acid groups, in polyphosphoric acid to form a solution or dispersion;;
 - B) optionally heating the solution or dispersion obtained according to step A) under inert gas to temperatures of up to 350°C to form the polyazole polymer;;

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- C) applying a layer using the mixture from step A) or B) to an electrode, thus forming a membrane on the electrode; and
- D) partially hydrolyzing the polyphosphoric acid moieties of the electrode membrane formed in step C) until the membrane it has a surface hardness.

55. The electrode of Claim 54, wherein the coating has a thickness of from 2 to 3000 μm .

56. A membrane-electrode unit comprising at least one electrode and at least one membrane as claimed in Claim 29.

57. A membrane-electrode unit comprising at least one electrode having a proton-conducting polymer coating which is based on polyazoles and is prepared by the following steps:

- A) mixing one or more aromatic or heteroaromatic tetraamino compounds with one or more aromatic or heteroaromatic carboxylic acids or derivatives thereof which contain at least two acid groups per carboxylic acid monomer, with at least part of the tetraamino compounds or the carboxylic acids comprising at least one phosphonic acid group, or mixing of one or more aromatic or heteroaromatic diaminocarboxylic acids, of which at least part comprises phosphonic acid groups, in polyphosphoric acid to form a solution or dispersion;
- B) optionally heating the solution or dispersion obtained according to step A) under inert gas to

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temperatures of up to 350°C to form the
polyazole polymer;

- 5 C) applying a layer using the mixture from step A) or B) to an
electrode, thus forming a membrane on the
electrode; and
- 10 D) partially hydrolyzing the polyphosphoric acid moieties of the
electrode membrane formed in step C) until the
membrane it has a surface hardness, and
partially hydrolyzing the polyphosphoric acid
moieties of at least one membrane as claimed
in Claim 29.

58. A fuel cell comprising one or more membrane-electrode units as
claimed in Claim 57.